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Methods for Determining Sources of Mercury Vapor in the Workplace

By D. L. Neylan, H. C. Triantafillou, and S. L. Law

UNITED STATES DEPARTMENT OF THE INTERIOR

Information Circular 8921

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UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

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CONTENTS

	Page
Abstract	1
Introduction	1
Chemical spot tests	2
Sensitivity	7
Reagent shelf life	7
Spot test techniques	8
Selected spot tests	9
Mercury vapor test papers	10
Portable mercury vapor detectors	11
Portable analytical instruments	13
Conclusions	14
References	15

ILLUSTRATION

1.	Gold-film analyzer for locating sources of mercury vapor	12

TABLES

1.	Reagents for mercury detection	2
2.	Portable mercury vapor detection devices	11
3.	Portable analytical instruments	13

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mg/m^3	milligram per cubic meter
g	gram	mm	millimeter
m^3	cubic meter	nm	nanometer
mg	milligram	µg	microgram
mL	milliliter	µL	microliter

METHODS FOR DETERMINING SOURCES OF MERCURY VAPOR IN THE WORKPLACE

By D. L. Neylan,[1] H. C. Triantafillou,[2] and S. L. Law[3]

ABSTRACT

The Bureau of Mines evaluated various methods for identifying sources of mercury vapor in excess of the threshold limit value (TLV) of 0.05 mg of mercury per cubic meter of air set by the American Council of Government and Industrial Hygienists (ACGIH) for mines and mineral processing plants. Chemical spot tests and portable devices for mercury determination were evaluated, based on information from published sources and performance in laboratory tests. Among the parameters examined were sensitivity, interferences, cost, ease of use, and other factors pertinent to field application. More than 50 methods were evaluated.

The investigators found that many readily available methods are suitable for identifying sources of mercury vapor in mines and mineral processing plants. The best method appears to be one that uses a commercially available mercury test paper sensitive only to mercuric ions.

For some of the more promising chemical spot tests, this report includes step-by-step instructions for field application.

INTRODUCTION

In order to enable the mining and mineral processing industry to comply with Federal regulations and to ensure workers' health, portable methods are needed for the on-site identification of sources of mercury vapor. In this report, many such methods are evaluated.

Although the TLV for mercury vapor in mines and mineral processing plants is set by ACGIH, Part 30 of the Code of Federal Regulations assigns enforcement of this limit to the Mine Safety and Health Administration (MSHA). At MSHA's request, the Bureau undertook the evaluation of chemical spot tests and instrumental methods for mercury determination described in this report. A commercially available mercury test paper evaluated by the Bureau as the best indicator for mercury is currently under study by MSHA for possible routine use in mine and mineral processing plant inspections.

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CHEMICAL SPOT TESTS

Spot tests are portable, provide on-site results, and are less expensive than other qualitative methods for determining the presence of metal ions. Because spot tests offer these advantages, the Bureau evaluated more than 50 spot test reagents to determine their suitability for identifying sources of mercury vapor in mines and mineral processing plants. These reagents are listed in table 1. For each reagent, the table lists the positive results observed when mercury is present, sensitivities, and interferences.

Generally, chemical reagents will not react directly with mercury or undissolved minerals containing mercury. Therefore, dissolution of some of the mercury-containing material with an appropriate acid is usually the first step in a chemical spot test. To achieve the desired test reaction, it may also be necessary to further adjust the dissolved mercury to the mercuric or mercurous valence state, adjust the acidity of the mercury and acid solution, or take other steps. The references in the last column of table 1 provide the guidance needed to perform spot tests using each of the listed reagents, and for some of the reagents an additional source of information is cited.

Table 1 does not list all the reported chemical methods for detecting mercury; only those for which sensitivities could be found are listed. Additional tests are mentioned by Feigl (2),[4] Welcher (11-14), and others. However, most, if not all, of the tests in popular use are summarized in table 1.

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Reagents for mercury detection

Reagent[1]	Reaction indicative of mercury	Sensitivity, μg Hg	Comments	References[2]
ORGANIC REAGENTS				
Acridine thiocyanate[3].	Yellow needles....	0.5	Yellow crystals also formed by Bi, Cd, U, Zn.	13
Allyl alcohol[3,4].....	Dark precipitate..	100	Reacts only with Hg^{+} ion.	11
Anthranilic acid.....	Colorless needles.	.06	Precipitates also formed by Ag, Ce, Co, Cu, Fe, Pd, Zn.	12
Benzopurpurin 4B.....	Reddish-violet color with Hg_2^{2+}; bluish-gray ring with Hg^{2+}.	40 15	Also reacts with Ag, Al, Mg, U.	14
Bromphenol blue.....	Yellow spot.....	20	Forms a violet-red ring with Pb.	14
Brucine[3].....	Crystals or precipitate.	.5	Also reacts with As, Bi, Cd, Ce, Cr, Cu, Pb, Sn, Zn, and others.	14

See footnotes at end of table.

TABLE 1. - Reagents for mercury detection--Continued

Reagent[1]	Reaction indicative of mercury	Sensitivity, μg Hg	Comments	References[2]
ORGANIC REAGENTS--Continued				
Cacotheline.....	Pink to red color.	.1	Also reacts with Ag, Au, Cu, Os, Pd. Ammonium chlorstannate causes the color.	14
2-Carboxyphenyl-5-azo-8-hydroxyquinoline.	Rose-violet precipitate.	200	Also reacts with Ag, As, Co, Cr, Cu, Ni, Pd.	11
Chromotropic acid.....	Bright yellow precipitate.	10	Ag, Fe, Ti interfere. No reaction with mercury chlorides.	2, 11
2,3-Diaminophenazine..	Red precipitate...	10	Also reacts with Cu. Fe and ammonia interfere.	12
Diethylaminophenyliminocamphor.	Rich pink or scarlet color.	20	Color from Hg^{2+} vanishes upon exposure to ammonia; color from Hg_2^{2+} turns black upon exposure to ammonia. Also reacts with Ag and Bi.	13
ρ-Dimethylaminobenzalrhodanine.	Red-violet color or precipitate.	.33	In the presence of chlorides, acetate must be added. Also reacts with Ag and Cu.	13
Dimethylaminophenyliminocamphor.	Rich pink or scarlet color.	20	Color from Hg^{2+} vanishes and color from Hg_2^{2+} turns black upon exposure to ammonia. Also reacts with Ag and Bi.	13
Di-α-naphthylcarbazone.	Gray-violet color.	.05	Also reacts with Cd, Cu, Fe, Mo.	13
Di-β-naphthylcarbazone.	Violet color.....	.015	.....do.....	13
Di-(O-nitrophenyl) carbazone.	Gray-blue color...	.08	Also reacts with Cu, Fe, Mo.	13

See footnotes at end of table.

TABLE 1. - Reagents for mercury detection--Continued

Reagent[1]	Reaction indicative of mercury	Sensitivity, µg Hg	Comments	References[2]
ORGANIC REAGENTS--Continued				
Di-(m-nitrophenyl) carbazone.	Red-brown color...	.05	Also reacts with Cu, Fe, Mo.	13
Di-(p-nitrophenyl) carbazone.	Blue color.....	.025	.....do.....	13
Diphenylcarbazide.....	Violet or blue precipitate.	1	Also reacts with Cd, Cr, Cu, Mo. Chlorides interfere.	2, 13
Diphenylcarbazone.....	.....do.....	.05	Also reacts with Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn.	2, 13
Dipicrylamine[4].....	Yellow or brown crystals.	400	Also reacts with Al, Be, Co, Cr, Cu, Fe, Ni, Zr.	14
Dithizone[3].....	Orange color.....	.25	Reacts with many metal ions. In acid solution, Au, Bi, Cu, Pt metals, Sb, Sn are main interferents.	2, 13
Erythrosin.....	Pink precipitate..	10,000	Reacts only with Hg_2^{2+}.	14
Hexamethylenetetramine.[5]	Light yellow color	.035	Color results from addition of iodide. Also reacts with Ca, Li, Mg, others.	13
Hoffman violet 3R.....	Gray precipitate..	10,000	Reaction is with Hg_2^{2+} ions. Also reacts with Sb and Sn.	14
Methylene blue iodide.	Blue color.....	.021	Also reacts with Ag and Sn.	14
α-Naphthylamine[3,5]....	Yellow precipitate	37	Also reacts with Cr, Cu, Au, W, others.	12
o-Nitrosophenol[3,4]....	Reddish-violet solid.	.1	Reacts only with Hg^{2+}; similar results with Cu^{2+}, Ni, Zn, Fe^{2+}.	13

See footnotes at end of table.

TABLE 1. - Reagents for mercury detection--Continued

Reagent[1]	Reaction indicative of mercury	Sensitivity, μg Hg	Comments	References[2]
ORGANIC REAGENTS--Continued				
Phenyl-5-azo-8-hydroxyquinoline.	Violet precipitate	100	Also reacts with Cu, Au, Mo, Ni, Pd, Zn.	11
Phenylhydrazinephenylthiocarbazinate.[3]	Reddish-purple precipitate.	10	Excess reagent must be avoided. CrO_4^{2-}, MoO_4^{2-}, VO_3^- interfere.	14
Phenylthiodantoic acid	Yellow precipitate	5	Similar results are obtained with Cu, Bi, Sb.	14
Phenylthiourea.....	Grayish-black precipitate.	20	Reaction is with Hg_2^{2+} ion. Sensitivity of 20 μg is for Hg_2^{2+}; sensitivity for Hg^{2+} is 1,000 μg. Also reacts with Ag, Cu^+, Au^{3+}, Pd^{2+}, Pt^{4+}.	14
Phenylurazole.....	Red precipitate...	20	Reacts in the presence of sodium acetate.	13
Phloroglucinol[3].....	.....do.....	20	Br^-, Cl^-, I^-, CN^-, SCN^- interfere. Also reacts with Cr, Fe, Sb, Sn.	11
Picric acid[3,4].....	Yellow precipitate	.15	Also reacts with Ba, Cd, Cu, Fe, Ni, Ag, and many others.	14
Purpuric acid.....	Red precipitate...	4,000	Forms a violet precipitate with Ag.	13
Quinoline[5].....	Colorless needles.	.32	Also reacts with Bi, Cd, Co, Sn, and others.	13
Rhodamine B[5].....	Dark red precipitate.	1,000	Also reacts with Au, Bi, Mo, Sb, W, and others.	14
Sodium diethyldithiocarbamate.	Brown plates.....	100	Reaction is with Hg^{2+}. Also reacts with Cd, Co, Mn, Pb, Sr, Zn.	14

See footnotes at end of table.

TABLE 1. - Reagents for mercury detection--Continued

Reagent[1]	Reaction indicative of mercury	Sensitivity, µg Hg	Comments	References[2]
ORGANIC REAGENTS--Continued				
Sozoiodol[3].....	Yellow precipitate	5	Reaction is with Hg_2^{2+}. Also reacts with Ag, Pb, Tl, NO_2^-.	11
5-(p-Sulfophenylazo)-8-hydroxyquinoline.	Bright red precipitate.	50	Cl^- interferes. Reacts also with Cu, Ni, Pd.	11
Tannin[3,5].....	Yellow-white precipitate.	10,000	Reacts with many ionic species.	12
Tetramethyl-p-phenylenediamine (Wurster's reagent).[3]	Violet precipitate	1	Also reacts with Ag, Cu, Fe, Os.	12
Urobilin.....	Rose-colored solution.	1	Also reacts with Cu, Zn.	14
INORGANIC REAGENTS				
Aluminum.....	Red color.....	0.0001	Neutral solution needed. Hg is amalgamated with Al using current from a flashlight battery; alumina formed gives red color with Alizarin.	2
Cuprous iodide.....	Deep red to orange color.	.003	Oxidants, Ag, Au, Mo, Pd, Pt, W interfere.	2
Hydrogen sulfide and formic acid.[3]	Colored colloidal suspension.	10	Also reacts with As and Pb. Colorimeter used for detection.	12
Hypophosphite-tin-IV..	Red or light pink color.	.1	Cacotheline used to form color with tin-II. Ag, Os, and noble metals interfere.	2
Iodine-starch[3].....	Absence of blue color in test solution.	.14	Same reaction with Ag.	14
Iodine-toluene[3].....	Red color.....	.02	I_2 is dissolved in equal amounts of ethanol and toluene.	11

See footnotes at end of table.

TABLE 1. - Reagents for mercury detection--Continued

Reagent[1]	Reaction indicative of mercury	Sensitivity, μg Hg	Comments	References[2]
INORGANIC REAGENTS--Continued				
Potassium dichromate-pyridine.[3,5]	Orange crystals...	.075	Both Hg_2^{2+} and Hg^{2+} cause the reaction.	13
Potassium iodide-glycerol.	Black precipitate.	50	Ag, Pb, Tl also precipitate with iodide, but are avoided in the test.	11
Stannous chloride-aniline.[3]	Brown, gray, or black precipitate.	1	Aniline is used to provide proper alkalinity and avoid Sb interference. Ag may interfere.	2

[1]All reagents should be considered hazardous. Before use, properties such as toxicity, carcinogenicity, explosibility, etc., should be determined by consulting such references as "Cancer Causing Chemicals" by N. I. Sax (Van Nostrand-Reinhold, New York, 1981, 466 pp.), "Dangerous Properties of Industrial Materials" by N. I. Sax (Van Nostrand-Reinhold, New York, 5th ed., 1979, 1258 pp.), "Handbook of Reactive Chemical Hazards" by L. Bretherick (CRC Press, Inc., Boca Raton, Fla., 1975, 976 pp.), and "The Merck Index" (Merck and Co., Inc., Rahway, N.J., 9th ed., 1976, 1313 pp.). For the reagents listed above, no listed hazards were found except as otherwise noted.

[2]For each reagent, these references generally give the chemical symbol, molecular weight, alternate nomenclature, and guidance for performing spot tests; for the less common organic compounds, preparation procedures are also given.

[3]Has toxic properties ranging from irritant to highly poisonous.

[4]Explosive or flammable.

[5]Possible or known carcinogen.

SENSITIVITY

The sensitivities of the spot test reagents listed in table 1 range from 0.0001 to 10,000 μg. If the mercury to be determined is in a form that dissolves slowly in acid, the more sensitive reagents are recommended because they minimize the time needed to obtain a positive test. However, if a reagent is to be used to locate fine droplets of a mercury spill, and low levels of mercury or mercury compounds with low solubility are not of interest, it may be better to use one of the less sensitive reagents that will test positive only for relatively high levels of dissolved mercury. For example, a reagent sensitive to mercury at the 10,000-μg level will detect--though perhaps with a weak color change--a droplet of mercury (density 13.6 g/cm^3) that is only 0.0007 cm^3 in volume.

For locating sources of mercury vapor in the workplace, test reagents of intermediate sensitivities are recommended. Their use avoids positive results for trace amounts of mercury but produces strong color changes for readily soluble forms of mercury at part-per-million levels of concentration.

REAGENT SHELF LIFE

Several of the reagents listed in table 1 need to be prepared fresh daily because they deteriorate rapidly upon exposure to actinic light (ultraviolet radiation capable of initiating photochemical reactions) or oxidation by air. These reagents would not generally

be considered for field applications. In laboratory testing of various reagents, it was found that chromotropic acid, Wurster's reagent (tetramethyl-p-phenylenediamine), and dithizone continued to give positive results for over 4 weeks after preparation if stored in low-actinic-glass (colored glass that absorbs actinic light) containers and kept out of direct sunlight. When stored in clear glass containers, all three were ineffective within 4 days of preparation. Dithizone changed to an ineffective yellow solution after only 1 day of exposure to sunlight. By comparison, symdiphenyl carbazide showed no effect from exposure to the direct sunlight. As a rule of thumb, all reagents should be prepared fresh, kept away from heat, and stored or carried in light-opaque, tightly stoppered containers. Proper safety containers should be used for the few reagents that require flammable organic solvents of high vapor pressure.

SPOT TEST TECHNIQUES

Chapters 1 and 2 of Feigl's text on spot tests (2) give a thorough overview of various techniques used in conducting spot tests. Some general guidelines are given in this section for the tests selected by the Bureau for mercury detection.

As mentioned in the previous section, low-actinic containers should be used for the organic reagents to retard deterioration. In the field, it is recommended that amber polyethylene dropping bottles with screw-cap tops be used. Even so, many of the organic reagents need to be prepared fresh for reliable results. Low-actinic containers are not needed for the 1:1 nitric acid used to dissolve the mercury for each test, but the container should be acid resistant. A Teflon[5] fluorinated ethylene propylene (FEP) dropping bottle or a drop dispensing bottle with a screw-cap top is useful for this purpose.

[5]Reference to specific trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

It is important that the tip of the eyedropper pipet used to deliver the reagents remain free from contamination. The tip of the pipet should not be touched against the receiving surface. The pipet tip should be no more than 1 or 2 cm above the place where the drop is to be delivered to assure accurate delivery and avoid splashing, but the drops should be allowed to fall freely. Not only does this technique avoid contamination, but the size of the drops remains fairly uniform, thereby allowing a semiquantitative comparison of mercury in the samples based on color intensities.

Direct testing on surfaces in a mill or mine is generally not possible nor desirable. A portion of the dust or material to be tested should be scraped from the surface with a spatula and placed on a filter paper or in a white glazed spot plate, a watch glass, or a micro test tube for attack by the 1:1 nitric acid. The acid is diluted with distilled water, generally by a factor of 3, before it is combined with the color-producing reagent. If the mercury is dissolved in a container other than filter paper, some of the liquid is then transferred to a white filter paper using an eyedropper pipet. If cotton is placed in the tip of the pipet, it will separate the liquid from the solids for a more interference-free observation of the color change. However, this separation is not usually necessary because the solution containing the dissolved mercury will diffuse away from the solids through the capillaries of the paper. The color-producing reagent is added to the solvent-moistened portion of the paper around the solids whether the solids are treated with the nitric acid directly on the paper or are transferred to the paper along with the solvent from a separate dissolution vessel.

The capillary action and adsorptive effects of filter paper make it the preferred substrate for spot reactions. Color reactions that appear to be relatively insensitive when diluted with the solvent in a spot plate or test tube may have excellent sensitivities on an

appropriate filter paper. This is because the colored, soluble, or insoluble reaction products of the test are held near the site of their production by the capillaries of the paper and are more readily seen because of the white background of the paper. Precipitation and filtration take place in the plane of the paper, resulting in a local enrichment and improved visibility of the colored reaction product.

When the mercury is dissolved from the sample directly on the filter paper, as recommended for some procedures, an acid-hardened paper such as Whatman 50 or Schleicher and Schuell 576 is recommended. These papers have a slow filtering speed, resulting in increased acid contact with the sample; they are acid-resistant; and they retain very fine precipitates on their smooth, white, lint-free surfaces for easy observation.

SELECTED SPOT TESTS

From the spot tests for mercuric ions listed in table 1, the Bureau selected the four tests described below as representative of those applicable to convenient field testing for sources of mercury vapor in the workplace. These tests were selected because of their simplicity, sensitivities, minimal interferences, and strong positive color changes in the presence of mercury.

The sample size for each test is approximately half of a 3- by 10-mm spatula spoonful. The mercuric ions for each test are obtained by dissolution of mercury metal or compounds from the sample using 1:1 nitric acid prepared by adding 50 mL of reagent-grade concentrated nitric acid to 50 mL of distilled water. All chemicals should be reagent grade and prepared with distilled water. Once prepared, the reagents should be tested with a blank 1:1 nitric acid sample for mercury contamination.

Cuprous Iodide Test

Reagents

1. Potassium iodide-sodium sulfite solution: 5 g KI and 20 g $Na_2SO_3 \cdot 7H_2O$ in 100 mL water.

2. Copper sulfate solution: 5 g $CuSO_4 \cdot 5H_2O$ in 100 mL 1*N* hydrochloric acid (83 mL reagent-grade concentrated hydrochloric acid diluted to 1 L with distilled water).

Reagent Paper

The filter paper is impregnated with the reactive reagents in the laboratory, minimizing the chemicals needed in the field. This is done by soaking an absorbent filter paper (e.g., Schleicher and Schuell 598 or Whatman 1) in the potassium iodide-sodium sulfite solution and then in the copper sulfate solution. The excess reagents are rinsed from the papers, and the papers are allowed to dry prior to their use in the field. The papers should last for several weeks if kept dry and if long exposure to direct sunlight or oxidizing environments is avoided.

Field Procedure

1. Add 1 or 2 drops of 1:1 nitric acid to the sample in a spot plate and let stand for 1 min.

2. Add 3 times as many drops of distilled water to dilute the acid.

3. Remove a portion of the liquid with an eyedropper pipet, and place a drop on the reagent paper. A red or orange color indicates the presence of mercury.

Diphenylcarbazide Test

Reagents

1. Diphenylcarbazide solution: 2 g diphenylcarbazide in 10 mL acetic acid and 10 mL ethanol. (Use low-actinic bottles. The solution is reddish-orange while effective.)

2. Sodium pyrophosphate solution: 3 g $Na_4P_2O_7 \cdot 10H_2O$ in 100 mL water.

3. 3 pct hydrogen peroxide solution if chromates may be present.

Field Procedure

1. Add 1 or 2 drops of 1:1 nitric acid to the sample on a filter paper and let stand for 1 min.

2. Add 3 times as many drops of distilled water to dilute the acid.

3. Add 2 drops of sodium pyrophosphate solution to eliminate interferences. If chromates are present, a drop of 3 pct hydrogen peroxide may also need to be added.

4. Add 1 drop of diphenylcarbazide solution at the edge of the solids. A violet or blue fleck indicates the presence of mercury.

Chromotropic Acid Test

Reagent

1. Chromotropic acid solution: 5 g sodium salt of chromotropic acid in 100 mL distilled water. (Use low-actinic bottle.)

Field Procedure

1. Add 1 or 2 drops of 1:1 nitric acid to the sample on a filter paper and let stand for 1 min.

2. Add 3 times as many drops of distilled water to dilute the acid.

3. Add 1 drop of chromotropic acid solution at the edge of the solids. A bright yellow color indicates the presence of mercury.

Commercial Test Paper

Description and Characteristics

A commercially available test paper sensitive only to Hg^{2+} ions is manufactured by Machery, Nagel and Co., Duren, West Germany, and is available in the United States from Gallard Schlesinger Chemical Mfg. Corp., Carle Place, N.Y. The cost is under $10 for 200 strips measuring 20 by 70 mm. No information is given by the manufacturer about the active ingredient in the paper. In the presence of Hg^{2+} ions, the grayish-brown paper turns white. If a capillary or micropipet is used to apply 10 to 20 µL of solution to the paper, a sensitivity limit of 25 mg Hg^{2+} per liter is obtained. Bureau tests with nitric acid solutions of Zn, Pb, Cu, Bi, and Cd did not produce a color change. This observation is in agreement with the manufacturer's claims that there are no interferences for this paper. MSHA has selected this test paper for field evaluation.

Field Procedure

1. Add 1 or 2 drops of 1:1 nitric acid to the sample in a spot plate and let stand for 1 min.

2. Add 3 times as many drops of distilled water to dilute the acid.

3. Touch a strip of the test paper to the liquid or use a capillary tube to touch the liquid to the paper. A white discoloration of the paper indicates the presence of mercury.

MERCURY VAPOR TEST PAPERS

Two test papers applicable for the direct detection of mercury vapor--as opposed to mercury ions, which are needed for reaction with most of the reagents listed in table 1--can be prepared in the laboratory. Filter paper impregnated with a 1 pct solution of palladium chloride and then dried provides a sensitive test for traces of mercury vapor in air (2). When mercury vapor comes in contact with the paper, the light brown color turns light gray to deep black. The stain can be made more visible by briefly holding the paper over concentrated ammonia. The formation of tetrammine palladium (II) chloride $[Pd(NH_3)_4Cl_2]$ changes the light brown paper to white, and the gray metallic palladium formed by the mercury vapor is easily seen against the white background. The most sensitive tests are obtained when the paper is completely dry.

A selenium sulfide test paper for mercury vapor can be prepared by bathing filter paper in a water solution of selenious acid, exposing the paper to

hydrogen sulfide, then washing and drying it (2). Black mercuric selenide and mercuric sulfide are formed when the selenium sulfide is exposed to mercury vapor.

Both mercury vapor test papers must be exposed to vapor for several hours if used as a passive monitor (7) in order to detect the 0.05 mg/m^3 TLV for mercury. Pumping the air across the test paper will shorten the time required for a positive test, and the degree of darkening of the selenium sulfide paper is proportional to the square root of the velocity of the air (7).

PORTABLE MERCURY VAPOR DETECTORS

Several portable, commercially available devices for mercury vapor detection are compared in table 2 for reliable measurement range, cost, and mode of mercury detection. Mercury vapor absorption of ultraviolet light at the 253.7-nm wavelength is the means of measuring relative concentrations for the Bacharach and Beckman instruments. Organic vapors, dust, or other components of the air that absorb ultraviolet light at the specified wavelength will give false indications of mercury, but generally this is not a problem. Background correction for broadband absorption could be added to the instrumentation, although this would add to the expense, bulk, and weight of the instrument.

TABLE 2. - Portable mercury vapor detection devices

Vendor	Model	Detection principle	Reliable measurement range,[1] mg Hg/m^3	Approximate cost (1982)
Bacharach Instrument Co., Pittsburgh, Pa. 15238.	MV-2	Hg vapor absorption of UV light.	0.01 - 0.2	$1,800
Beckman Instruments, Inc., Fullerton, Calif. 92634.	K-23	.....do.....	.005- 1	2,200
Bendix Corp., Largo, Fla. 33543.	Tube 40	Absorption of Hg in a tube causes cupric iodide color change to orange.	.05 -13	200
Jerome Instrument Co., Concord, N.H. 03301.	401	Absorption of Hg by Au film increases electrical resistance.	.01- .5	3,000
Mine Safety Appliances, Pittsburgh, Pa. 15235.	C-210	Absorption of Hg by iodine-impregnated charcoal; Hg determined by laboratory analysis.	.01- .3	400
National Draeger, Inc., Pittsburgh, Pa. 15235.	Mercury	Absorption of Hg in a tube causes cupric iodide color change to orange.	.1- 2	400
3M Co., St. Paul, Minn. 55101.	[2]3600	Absorption of Hg by an Au film which is sent to manufacturer for analysis.	.005- .20	([3])

[1]Actual detection limits are generally lower than the lowest values given for reliable measurement.

[2]Personnel mercury vapor monitor (film badge).

[3]$160 for 5 film badges.

The Jerome instrument (fig. 1) works on the principle that the electrical conductivity of a gold film changes as it forms an amalgam with mercury vapor from the air (6, 8). Interference by dust, organic vapors, or other air components is avoided unless a vapor that is reactive with gold, e.g., chlorine, is present. The 3M Co.'s personnel film badge monitors also work on the principle of mercury collection by gold, but the mercury is measured in the lab using electrical resistivity (5).

The remaining three mercury vapor detection systems listed in table 2--sold by Bendix Corp., Mine Safety Appliances, and National Draeger, Inc.--use the chemical reaction of mercury with iodine to detect the vapor. In the Bendix and National Draeger absorption tubes, the red to orange color of the cuprotetraiodomercuriate is the indicator of the presence of mercury vapor. The Mine Safety Appliances system uses iodine impregnated charcoal to trap the mercury, which must then be chemically eluted from the charcoal and determined in the laboratory. Although the lower limit of the reliable measurement range of the National Draeger tube is 0.1 mg/m^3, the actual detection limit--the level at which the characteristic red coloring begins to appear--is below the 0.05 mg/m^3 TLV set by ACGIH. A comparative study of personal mercury sampling devices has been reported by McCammon (4).

FIGURE 1. - Gold-film analyzer for locating sources of mercury vapor.

For the purpose of on-site location of mercury vapor sources, the need to return to the laboratory for mercury determination would eliminate from consideration the 3M Co. and Mine Safety Appliances detectors. The absorption tubes sold by Bendix and by National Draeger show a cumulative mercury level, with the red color advancing through the tube with continued exposure to mercury vapor, and therefore lack the ability to show fluctuations in mercury vapor concentrations from one minute to the next as the device is moved from place to place. The most useful devices for the intended purpose are the more expensive battery-powered ultraviolet and gold-film-resistivity instruments. Each instrument has a survey mode that continuously samples the air, denoting areas of high mercury concentration near sources of mercury vapor contamination.

PORTABLE ANALYTICAL INSTRUMENTS

The portable analytical instruments listed in table 3 have the capability, except for the Perkin-Elmer (formerly Coleman) model MAS-50A, of determining other elements in addition to mercury. The MAS-50A is designed specifically for the cold-vapor atomic-absorption determination of mercury (1).

Samples must be taken from the area being surveyed before instrumental analysis can be performed using the MAS-50A. This is true also for the Graphic Controls ion-selective electrode and the Hach Chemical ultraviolet spectrophotometer. In each case the mercury must be dissolved from the sample and chemically treated. When the cold-vapor atomic-absorption method is used, the mercuric ion is reduced to the metallic state and then vaporized so that mercury can be determined by atomic absorption at the 253.7-nm wavelength. The ion-selective electrode method uses a sensing component for the direct determination of mercuric ion activity, or the mercuric ion may be determined indirectly by titration with iodide until an excess of iodide is detected by an iodide-selective electrode (10). However, accurate determination of mercury using the ion-selective electrode may be difficult because of interferences from chloride, bromide, iodide, cyanide, thiocyanates, sulfide, and silver. The ultraviolet spectrophotometric method is

TABLE 3. - Portable analytical instruments

Vendor	Model	Type of instrument	Approximate cost (1982)
Columbia Scientific, Austin, Tex. 78766.	700	X-ray spectrometer.....	$8,000
Graphic Controls Corp., Buffalo, N.Y. 14240.	PHI 96100	Ion-selective electrode..	300
Hach Chemical Co., Loveland, Colo. 80537.	DR/2	UV spectrophotometer.....	750
Panametrics, Inc., Waltham, Mass. 02154.	Panalyzer 4000	X-ray spectrometer.....	6,400
Perkin-Elmer Corp., Oakbrook, Ill. 60521.	MAS-50A	Cold-vapor atomic absorption analyzer.	2,400

indirect: Dithizone is used as the active ingredient to complex the mercuric ions, and the complex is then extracted into chloroform (3). The mercury concentration is determined at the point where an excess of dithizone gives an absorbance at the 610-nm wavelength. (For an indication of the many interferences that are possible when dithizone is used, see table 1). The usefulness of any of these three techniques (cold-vapor atomic absorption, ion-selective electrode, and ultraviolet spectrophotometric) for on-site location of mercury vapor sources is greatly restricted by the need to collect samples and chemically treat the samples to obtain results.

The utility of fluorescent X-ray spectrography for determining trace concentrations of heavy metals in various matrixes is well documented. The development of portable X-ray instrumentation has extended this application to in situ determinations of trace elements in ore samples (9). Mercury concentrations of 0.7 pct Hg in a 1-g sample can be determined. Sensitivity is a function of the detector resolution and the activity of the radioisotope used for sample excitation.

The type of detector used in a portable X-ray analyzer greatly affects both cost and sensitivity. Scintillation detectors and proportional counters have long been used to detect X-rays in analytical instruments. The two devices listed in table 3 use sealed proportional counters. They are rugged, inexpensive, and provide moderate sensitivity in portable devices when coupled with balanced filters to discriminate the X-rays of interest from a complex spectral background. Only one element is determined for each set of balanced filters.

The alternative approach is to use a device similar to the "X-site" alloy-sorting instrumentation marketed by Kevex Inc. This system uses a solid-state semiconductor detector (lithium-drifted silicon), and simultaneous multielement determinations are therefore possible. The probe head containing the detector is portable, but the required power supply and the computer hardware are not. The silicon detector gives the system greater flexibility for resolving complex spectra than a proportional counter has, but the detector requires constant liquid nitrogen cooling and costs much more than a proportional counter.

The only commercially available portable X-ray analyzer with a solid-state detector is a gold analyzer marketed by Ortec Inc. It has a germanium detector, requires liquid nitrogen cooling, and costs about $60,000. Its sensitivity for gold is less than 0.1 pct Au in ore samples, and its sensitivity for mercury is probably comparable, because gold and mercury X-rays have similar energies. The germanium detector is able to detect higher energy X-rays than the proportional counter, and fewer interferences exist for the K-alpha X-rays of mercury; therefore, consistently lower detection limits for mercury in different types of samples would be expected.

CONCLUSIONS

Of the more than 50 reagents for mercury identification spot tests that were examined, many could be applied for the identification of sources of mercury vapor in mines and mineral processing plants. Poor shelf life, nonselectivity, and lack of sensitivity would eliminate some from consideration. At least two spot tests that react to mercury vapor are available; the others require the presence of mercury ions for positive test results. One commercially available mercury test paper, sensitive only to mercuric ions, appears to best meet the need for locating sources of mercury vapor in the workplace.

Portable mercury vapor detectors that could be used for real-time surveying in a mine or mill range in cost from $1,800 to $3,000. Less expensive vapor detection devices require laboratory backup or cannot provide the flexibility needed to pinpoint a mercury vapor source.

Portable analytical instrumentation is also limited for field use by the need for sample collection, dissolution, and chemical treatment in every case except for the X-ray analyzers. However, the portable X-ray analyzers are the most expensive of all the detection systems examined, ranging from $6,000 to $8,000 or more.

Methods of identifying sources of mercury vapor in mines and mineral processing plants are readily available with no need for further research and development. The inexpensive, commercially available mercury test paper mentioned above appears to have no interferences and requires minimal skills to obtain reliable results.

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